Electronic properties of WTe_2 and $MoTe_2$ single crystals

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Electronic properties of WTe_2 and $MoTe_2$ single crystals

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Abstract. WTe_2 and $MoTe_2$ single crystals were grown, and their electrical resistivity in the temperature range from 80 K to 300 K, optical properties at room temperature in the spectral range of 0.17-5.0 eV were studied as well as theoretical calculations of the electronic structure were performed. It is shown that the temperature dependence of the electrical resistivity of orthorhombic WTe_2 has a metallic type with resistivity value of (0.5-1) mOhm·cm, while hexagonal $MoTe_2$ has a semiconductor one and resistivity value (0.5-1) Ohm·cm, which is three orders of magnitude larger than the resistivity of WTe_2. Optical properties indicated that there is no contribution from free carriers in the entire spectral range studied. The calculated densities of the electronic states of $MoTe_2$ and WTe_2 showed the presence of a bunch of the molybdenum and tungsten electronic states in a wide energy interval with strong admixing of tellurium states. In the WTe_2 compound, the larger number of the electronic states is located near the Fermi energy, characterizing a more metallic state in this compound as compared to $MoTe_2$.

1. Introduction

The transition metal dichalcogenides (TMDs) are a wide group of layered compounds with the chemical formula MX_2, where M is a transition metal (for example, Mo, W and V), X is a chalcogen (S, Se and Te). The properties of these materials are highly dependent on the composition and crystal symmetry, thus these materials have a wide range of different properties and are used in various applications [1], for instance, extremely large magnetoresistance [2], charge density waves [3], superconductivity [4], topological phase [5], optoelectronic devices [6]. It is known that TMDs WTe_2, $MoTe_2$ and their ternary compounds $Mo_xW_{1-x}Te_2$ can exhibit properties of topological Weyl semimetals (TWSs) [7-12]. These materials have unusual electronic states on the surface as well as in the bulk, which open a new era in condensed matter physics and lead to new potential applications. Weyl semimetals have massless Weyl fermions, chiral quasiparticles with «zero» effective mass and a linear dispersion law near Weyl nodes in the reciprocal space. Topological gapless surface states in TWSs are Fermi arcs, which are open curves and connect the projections of bulk Weyl nodes in surface Brillouin zone [13-16]. Massless Weyl fermions, that can be controlled much faster than conventional charge carriers, and spin-polarized Fermi arcs make Weyl semimetals promising for creating ultrafast electronic and spintronic devices.

TMDs $Mo_xW_{1-x}Te_2$ can crystallize into three polytypes under different experimental conditions with hexagonal (2H or α phase), monoclinic (T' or β phase) and orthorhombic (T_d or γ phase) lattices. Depending on the crystal structure, these compounds have very different electronic properties. In contrast to 2H-compounds having semiconductor properties, T' and T_d compounds are typical semimetals [1, 12, 17, 18]. Note that $MoTe_2$ can exist in 2H, T' and T_d phases, while the common structure of WTe_2 is orthorhombic.

Currently, there are papers devoted to theoretical and experimental studies of WTe_2 and $MoTe_2$ [2, 4, 7-10, 19-22]. However, it is interesting to carry out a comprehensive study of the electronic properties of both these compounds, namely, their electrical resistivity, optical properties, comparing with the theoretical calculations of the electronic structure.

2. Experimental

WTe_2 and $MoTe_2$ single crystals were grown by the chemical vapor transport method using Br_2 as a transport agent according to the method described in [23]. X-ray diffraction analysis revealed that WTe_2 crystallizes in an orthorhombic structure with the lattice parameters a = 3.435(8) Å, b = 6.312(7) Å, c = 14.070(4) Å, at the same time $MoTe_2$ crystallizes in a hexagonal structure with the lattice parameters a = 3.540(7) Å and c = 13.983(5) Å. The chemical composition of the samples was confirmed by X-ray microanalysis using a FEI Inspect F scanning electron microscope equipped with an EDAX attachment. The temperature dependences of the electrical resistivity $\rho(T)$ were measured by the standard method (see, e.g. [24, 25]) in the (*00l*) plane of the samples in the temperature range from 80 to 300 K. The optical constants, the refractive index n and the absorption coefficient k, were measured using the Beattie method with one reflection from the (*00l*) plane of the samples in the spectral range of 0.17–5.0 eV at room temperature. The measurement error was 2–4% in the visible and ultraviolet (VUV) regions and ~ 6% in the middle infrared (IR) region. The values of n and k were used to calculate the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the complex dielectric permittivity ε

$$\varepsilon_1(\omega) = n^2 - k^2, \tag{1}$$

$$\varepsilon_2(\omega) = 2nk, \tag{2}$$

the real part of the complex optical conductivity $\sigma(\omega)$

$$\sigma(\omega) = nk\omega / 2\pi, \tag{3}$$

(ω is the cyclic frequency of the light wave) and reflectivity R

$$R(\omega) = \frac{[(n-1)^2 + k^2]}{[(n+1)^2 + k^2]}. \tag{4}$$

3. Results and discussions

3.1. Electrical resistivity

Figure 1 shows the temperature dependences of the electrical resistivity $\rho(T)$ of WTe_2 and $MoTe_2$ single crystals. The temperature dependence of the electrical resistivity $\rho(T)$ of WTe_2 (figure 1(a)) is seen to have a metallic type, that is, the resistivity ρ increases with temperature. Resistivity value of WTe_2 is around (0.5–1) mOhm·cm, which is typical for semimetals. At the same time, the dependence $\rho(T)$ of $MoTe_2$ (figure 1(b)) shows a semiconductor behaviour with a quite high resistivity (0.5-1) Ohm·cm, which is typical for semiconductors. However, the curve $\rho(T)$ of $MoTe_2$ reveals the minimum of resistivity at T = 190 K, the nature of which is not completely clear.

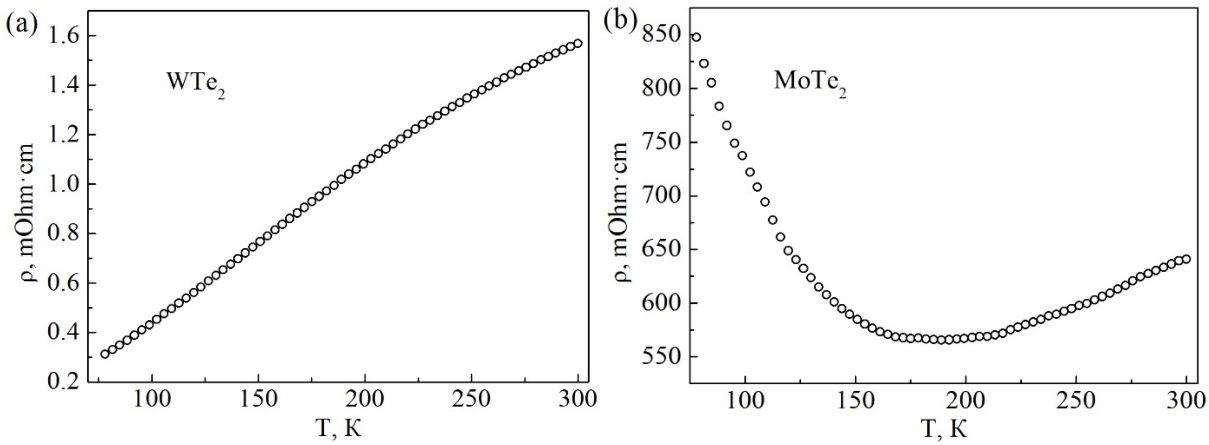

Figure 1. Temperature dependences of the electrical resistivity of WTe_2 (a) and $MoTe_2$ (b) single crystals.

3.2. Optical properties

Optical studies are presented in figures 2-3. It is known that the main role in the formation of optical properties in metals and alloys in the infrared region of the spectrum is played by the mechanism of intraband acceleration of electrons by the light wave field [26]. Negative values of the real part of the complex dielectric permittivity in the infrared region of the spectrum are the optical criterion for the metallic conductivity type of a substance. Interband absorption, that is, the quantum absorption of light with the transfer of electrons from lower energy states to free upper states, which gives information about the electron energy spectrum, dominates in the visible and ultraviolet regions. The complex dielectric permittivity ε is the sum of the contributions from the intraband and interband absorption mechanisms that can coexist in a certain energy range. Graphs of the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the complex dielectric permittivity ε of WTe_2 and $MoTe_2$ single crystals are shown in figure 2. In the infrared region of the spectrum, low values of the imaginary part ε_2 and positive values of the real part ε_1 of the complex dielectric permittivity ε can be noted, which suggests that there is no contribution from free carriers up to the boundary of the investigated range of 0.2 eV.

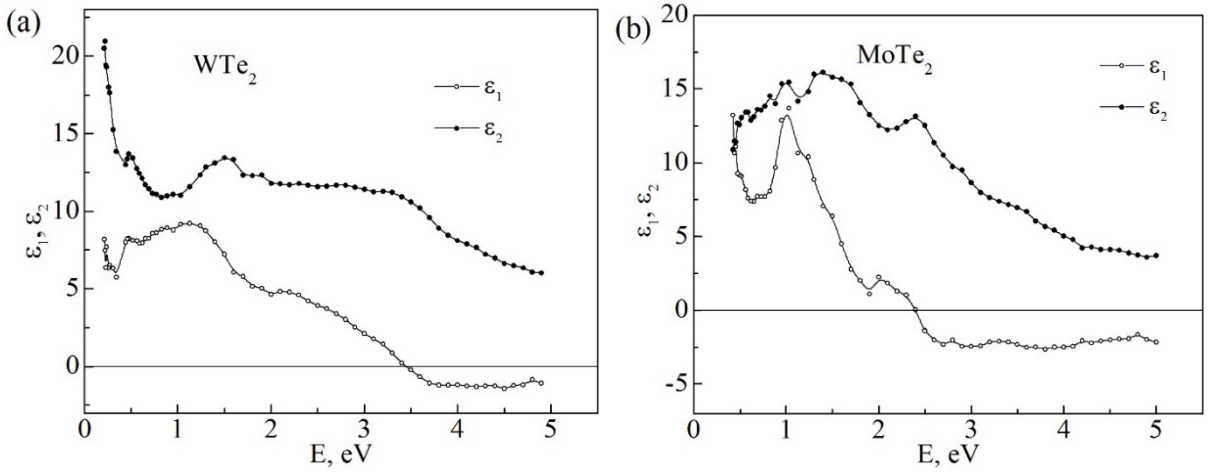

Figure 2. Dispersions of the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the complex dielectric permittivity of the WTe_2 (a) and $MoTe_2$ (b) single crystals.

Figure 3 shows the optical conductivity curves of WTe_2 and $MoTe_2$ single crystals. In the studied range, the optical conductivity spectrum $\sigma(\omega)$ of these compounds is one broad band centered at

3.4 eV and 2.4 eV, respectively, formed by interband transitions. In the limit $\omega \rightarrow 0$, the optical conductivity is known to approach the static value $\sigma_0 = 1/\rho_{300K}$ (where ρ_{300K} is electrical resistivity at room temperature). The static conductivity values of WTe_2 (figure 3(a)) and $MoTe_2$ (figure 3(b)) are marked on the ordinate axis as $5.74 \cdot 10^{14}$ s^{-1} (637.80 $(Ohm \cdot cm)^{-1}$) and $1.40 \cdot 10^{12}$ s^{-1} (1.56 $(Ohm \cdot cm)^{-1}$), respectively.

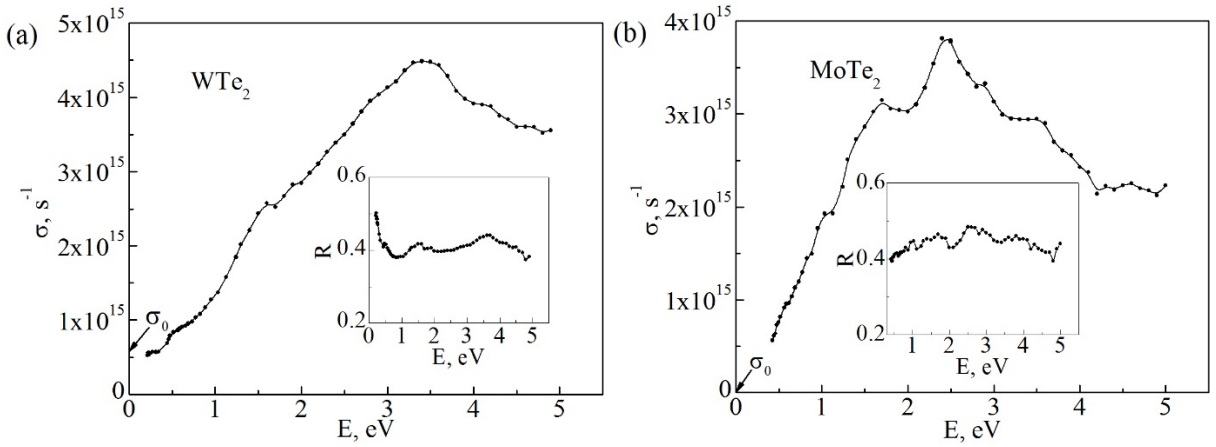

Figure 3. Dispersions of the optical conductivity $\sigma(\omega)$ of WTe_2 (a) and $MoTe_2$ (b) single crystals. The insets show the dispersions of the reflectivity *R*.

The reflectivity *R* has low values for both compounds, varying from 0.37 in the ultraviolet region of the spectrum to 0.5 in the infrared one for WTe_2 (insert in figure 3(a)), and from 0.39 to 0.48 for $MoTe_2$ (insert in figure 3(b)).

3.3. Electronic structure calculations

Theoretical calculations of the electronic structure of $MoTe_2$ and WTe_2 compounds were performed using the TB-LMTO-ASA computer software package based on the method of linearized muffin-tin (MT) orbitals in the approximation of atomic spheres. The electronic structure was obtained as a result of self-consistent calculations in the framework of the approximation of the local electron spin density. Integration was carried out over a grid of k-points in the reciprocal space with a total number of $6 \times 6 \times 2$ points by the tetrahedron method. The orbital basis included the muffin-tin orbitals corresponding to the 6s-, 6p-, 5d- states of W, 5s-, 5p- states of the tellurium ions, as well as the 5s-, 5p-, and 4d- states of the molybdenum ions. The radius of the MT-spheres of molybdenum and tungsten was 2.9 a.u., the radius of the MT-sphere of tellurium was 3.0–3.2 a.u. Empty spheres were added in the calculations to fill the cell volume. The absence of moments on the W and Mo ions was checked in the self-consistent calculations of the electronic structure, the obtained solution is completely nonmagnetic. The calculated densities of the electron states of $MoTe_2$ and WTe_2 are shown in figure 4 and reveal the presence of a bunch of the molybdenum and tungsten electronic states in a wide energy interval.

In the WTe_2 compound, the larger number of the electronic states is located near the Fermi energy, characterizing a more metallic state in this compound as compared to $MoTe_2$, which is consistent with the optical data. In order to more accurately describe the states near the Fermi level, to check for the presence of a pseudogap or a gap for different samples, a hybridization approach will be used that allows one to describe the energy gap in the layered MTe_2 samples (M = Mo and W). Strong admixing of tellurium states occurs in a wide energy interval. All the mentioned electronic states form a wide band of states.

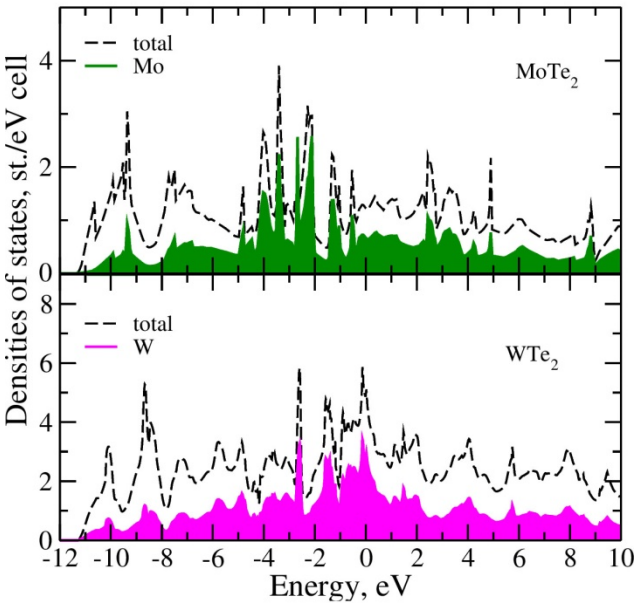

Figure 4. The theoretical densities of the electron states of $MoTe_2$ and WTe_2. The Fermi level is located at zero energy.

4. Conclusions

The studies of the electrical resistivity, optical properties of WTe_2 and $MoTe_2$ single crystals, as well as theoretical calculation of electronic structure of these compounds allow us to draw the following conclusions.

1. The temperature dependence of the electrical resistivity of orthorhombic WTe_2 single crystal has a metallic behavior, and the resistivity value is around (0.5–1) mOhm·cm. At the same time, the temperature dependence of electrical resistivity of hexagonal $MoTe_2$ has a semiconductor type with resistivity value of about (0.5–1) Ohm·cm, which is three order of magnitude larger than the resistivity of WTe_2.

2. Optical studies of WTe_2 and $MoTe_2$ single crystals showed that there is no contribution from free carriers in the entire spectral range studied. The optical conductivity spectrum of these compounds is one broad band, formed by interband transitions.

3. The calculated densities of the electronic states of $MoTe_2$ and WTe_2 revealed the presence of a bunch of the molybdenum and tungsten electronic states in a wide energy interval with strong admixing of the tellurium electronic states. In the WTe_2 compound, the larger number of the electronic states is located near the Fermi energy, which characterizes a more metallic state in this compound as compared to $MoTe_2$.

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